

【Type of Document】 Patent Application  
【Reference No. 】 97 YA 22  
【Date of Filing】 November 7, 1997  
【Addressee 】 Director-General of the Patent Office  
【International Patent Classification 】 B01J 35/00  
【Title 】 Resin Structure having Photocatalyst-Supporting Film  
Laminated Thereto  
【Numbers of Claims 】 16  
【Inventor】  
【Address or Place of Residence 】 c/o Odawara Research Center, Nippon  
Soda Co., Ltd., No. 345, Takada, Odawara-shi, Kanagawa  
【Name of Inventor】 KIMURA Nobuo  
【Inventor】  
【Address or Place of Residence 】 c/o Odawara Research Center, Nippon  
Soda Co., Ltd., No. 345, Takada, Odawara-shi, Kanagawa  
【Name of Inventor】 FUKAYAMA Shigemitsu  
【Inventor】  
【Address or Place of Residence 】 c/o Odawara Research Center, Nippon  
Soda Co., Ltd., No. 345, Takada, Odawara-shi, Kanagawa  
【Name of Inventor】 ONO Kazuo  
【Inventor】  
【Address or Place of Residence 】 c/o Nisso Jushi Co., Ltd., 1274,  
Isohara Isohara-cho, Kitaibaraki-shi, Ibaraki  
【Name of Inventor】 KATAOKA Masayuki  
【Inventor】  
【Address or Place of Residence 】 c/o Nisso Jushi Co., Ltd., 1274,  
Isohara Isohara-cho, Kitaibaraki-shi, Ibaraki  
【Name of Inventor】 OKABE Kazuji  
【Inventor】  
【Address or Place of Residence 】 c/o Nisso Jushi Co., Ltd., 1274,  
Isohara Isohara-cho, Kitaibaraki-shi, Ibaraki  
【Name of Inventor】 KOMODA Yoshiharu  
【Applicant 】  
【Registered No.】 000004307  
【Name of Applicant 】 Nippon Soda Co., Ltd.  
【Representative】 TSUKIHASHI Tamikata

**【Applicant 】**

**【Registered No. 】** 593088898  
**【Name of Applicant 】** Nisso Jushi Co., Ltd.  
**【Representative】** KANEHARA Hironori

**【Attorney】**

**【Registered No. 】** 100107984  
**【Patent Attorney 】**  
**【Name of Attorney】** HIROTA Masanori

**【Description of Fees 】**

**【Advanced Payment File No. 】** 044347  
**【Amount of Advanced Payment】** 21000

**【List of Articles Submitted】**

|                                 |                            |   |
|---------------------------------|----------------------------|---|
| <b>【Designation of Article】</b> | Specification              | 1 |
| <b>【Designation of Article】</b> | Drawing                    | 1 |
| <b>【Designation of Article】</b> | Abstract of the Disclosure | 1 |

**【Letter No. of Comprehensive Power of Attorney 】** 9700920

【Description of Document】 Specification

【Title of the Invention】 Resin Structure having Photocatalyst-Supporting Film Laminated Thereto

【Claims】

【Claim 1】 A resin structure laminated with a photocatalyst-supporting film characterized in that the resin structure is obtainable by laminating a photocatalyst-supporting film onto the surface of a resin substrate by applying heat-pressing and is having photocatalytic activity capable of decomposing triolein at a rate of  $5\mu\text{g}/\text{cm}^2/\text{day}$  or more under irradiation of UV rays in UV-A range at a strength of  $3\text{ mW}/\text{cm}^2$  and at an atmospheric temperature of  $25^\circ\text{C}$  and relative humidity of 70%.

【Claim 2】 The resin structure laminated with a photocatalyst-supporting film according to Claim 1 characterized in that the photocatalyst-supporting film is made of polymer resin film in which a photocatalyst layer is carried on the film via an adhesive layer.

【Claim 3】 The resin structure laminated with a photocatalyst-supporting film according to Claim 2 characterized in that the polymer resin film is a film on which 2 or more resin films are laminated.

【Claim 4】 The resin structure laminated with a photocatalyst-supporting film according to Claim 2 or Claim 3 characterized in that the polymer resin film is made of a resin selected from a group consisting of polycarbonate resins, copolymers of 2 or more of polymethylmetacrylate resins or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins.

【Claim 5】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 2 through 4 characterized in that the thickness of the polymer resin film is in a range of from 5 to  $200\mu\text{m}$ .

【Claim 6】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 2 through 5 characterized in that the adhesive layer is formed by coating a coating solution for an adhesive layer containing a silane coupler as a hardener.

【Claim 7】 The resin structure laminated with a photocatalyst-supporting film according to Claim 6 characterized in that a coating solution for an adhesive layer prepared by adding a silane coupler in an amount of 0.1-5% by weight relative to the weight of the coating

solution as a hardener to a coating solution composed of a silicon denaturated resin in an amount of 2-20% by weight which contains either polysiloxane in an amount of 10-50% by weight or colloidal silica in an amount of 5-30% by weight is used for the coating solution for an adhesive layer.

【Claim 8】 The resin structure laminated with a photocatalyst-supporting film according to Claim 6 characterized in that a coating solution prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight relative to the weight of the coating solution into a solution containing either monoalkyltrimethoxysilanes or its hydrolyzed product in an amount of 1-10% by weight and silica sol in an amount of 0.1-5% by weight is used as the coating solution for an adhesive layer.

【Claim 9】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 2 through 8 characterized in that the thickness of the adhesive layer is in a range of from 0.5 to 5  $\mu\text{m}$ .

【Claim 10】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 2 through 9 characterized in that the photocatalyst layer contains a metal oxide sol in an amount of 1-10% by weight as solid component and titanium dioxide in an amount of 1-10% by weight as solid component.

【Claim 11】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 2 through 9 characterized in that the photocatalyst layer contains silica sol in an amount of 1-10% by weight, either of monoalkyltrimethoxysilane or its hydrolyzed product in an amount of 1-10% by weight and titanium dioxide in an amount of 1-10% by weight.

【Claim 12】 The resin structure laminated with a photocatalyst-supporting film according to Claim 10 or Claim 11 characterized in that the thickness of the photocatalyst layer is in a range of from 0.1 to 5  $\mu\text{m}$ .

【Claim 13】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 1 through 12 characterized in that the resin substance is made of a resin selected from a group consisting of poly(vinyl chloride) resins, polyethyleneterephthalate

resins, polymethylmetacrylate resins, polycarbonate resins, polyethylene resins, polypropylene resins, shock-resistant denaturated polystyrene resins, and acryl-butadiene-styrene copolymers.

【Claim 14】 The resin structure laminated with a photocatalyst-supporting film according to any of Claims 1 through 13 characterized in that the shape of the resin substrate is plate-form, sheet-like, woven fabric-like, nonwoven fabric-like, resin-containing reinforced fabric-like or tubular.

【Claim 15】 A method for preparing the resin structure laminated with a photocatalyst-supporting film characterized in that the laminated resin structure is prepared firstly by coating a coating solution for an adhesive layer wherein a silane coupler as a hardener is added onto a polymer resin film and then drying it and subsequently coating a coating solution for a photocatalyst layer onto the adhesive layer and then drying it to prepare a photocatalyst-supporting film which carries the photocatalyst layer on the polymer resin film via the adhesive layer, and then laminating the photocatalyst-supporting film onto the surface of a resin substrate by applying heating and pressing.

【Claim 16】 Outdoor-use signboards and other signs, telephone box, materials for outdoor tents, washstands, modular bathes, systematic kitchens, water tanks for ornamental fishes, plastic cases, wall papers, food-use trays, and packaging films using the resin structure laminated with a photocatalyst-supporting film according to any of Claims 1 through 14 at least for the part of them.

#### 【Detailed Explanation of Invention】

##### 【0001】

##### 【Field of Invention】

The present invention is related to a resin structure, which is obtainable by laminating thereto a photocatalyst-supporting film having deodorant, antiflouling, antibacterial, antifungal and other effects by means of heat-pressing, a method for preparing such resin structure and various products for which such resin structure is applicable.

##### 【0002】

##### 【Prior Arts】

Titanium dioxide, which is n-type semiconductor, has been known as a photocatalyst that activates various chemical reactions with

ultraviolet radiation energy, such as chemical reactions resulted in during a process of pasteurization and decomposition of organic substance. On the other hand, various methods to carry a photocatalyst layer onto a glass plate, plastics, tiles, etc. have been proposed (See JP Laid-opened No. Sho 62-66861 and No. Hei 5-309267, EP 633064 and USP 4888101). However, a resin structure which is laminated with a photocatalyst-supporting film, particularly the one composed of widely-used polycarbonate resin or cloth-reinforced poly(vinyl chloride) resin and capable of carrying a photocatalyst without losing photocatalytic activity, has not been known. Further, a method to maintain deodorant, antifouling, antibacterial and antifungal effects for a long time by efficiently utilizing photocatalytic activity given by the resin structure being laminated with such photocatalyst-supporting film has not been reported.

【0003】

In the past, outdoor installed soundproof walls made of polycarbonate resin plates, a resin reinforced with poly(vinyl chloride)-absorbed fibers and the like get stained easily with dust and smoke, normally develop discoloration thereof and disfigure during a few months. Further, such soundproof walls gets mold growth thereon thanks to great amount of plasticizer components contained in poly(vinyl chloride) resin, and a method to coat a fluororesin onto the surface of such soundproof wall as a countermeasure. However, the coating of a fluororesin tends to increase the water repellent property on the surface and the oil affinity, which makes attaching of dust and smoke to the surface of such resin plates more easier. Based on the characteristic of titanium dioxide that appears to show hydrophilic property when it is subjected to ultraviolet rays in the atmosphere, a method to facilitate washing of attached oil components, such as oil mist, with water, particularly by raining, by making the surface of outdoor structure hydrophilic with titanium dioxide (See JP Laid-open No. 63-100042 gazette and WO 96/29375). This is to utilize a mechanism that the structure surface which becomes hydrophilic makes spreading of water on the surface easier, eventually allowing to float oil components from the surface and to fall down therefrom. However, according to the method disclosed in those gazettes, there is

practically a constrain in the application for soundproof walls for roads where great amount of stain, such as exhaust of diesel cars, tend to firmly attach to such walls.

**【0004】**

In WO 97-134 gazette, an example which enables to provide a resin structure having high photocatalytic activity and excellent durability prepared by means of carrying a photocatalyst layer composed of photocatalyst particles complex containing metal oxide gel thereon via an adhesive layer composed of acrylsilicon resin added with polysilixane by either dipping or spraying method is disclosed. However, according to this invention, though it enables to provide a photocatalyst-supporting film of which reverse side is coated with a sticking agent, there is a disadvantage that photocatalytic activity deteriorates when the film is subjected to laminating process by heat-pressing, that coating of a photocatalyst at high speed film formation get problematic due to insufficient hardening of an adhesive layer.

**【0005】**

A photocatalyst-supporting film prepared by providing a photocatalyst layer composed of a photocatalyst complex containing a metal oxide gel via an adhesive layer composed of an acrylsilicon resin added with polysiloxane onto a polyester film and is capable of maintaining high photocatalytic activity and excellent durability is disclosed in WO 97-134. However, it is generally difficult to laminate the polyester film by means of heat-pressing and such film cannot be used for the purpose according to the present invention.

**【0006】**

In addition, with the composition of the disclosed coating solution in WO 97-134, there is a disadvantage that the coated film tend to attache to the reverse side thereof due to insufficient drying and hardening of the coated layer during high speed film formation. In particular, a film which can be laminated by heat-pressing has low temperature property as to thermal resistance and thermal deformation as low as 100 °C, it is difficult to carry out high speed formation of a film which is applicable for heat-laminating process by using the coating solution and coating method disclosed in WO 97-134, and photocatalytic activity may disappear depending upon the condition of

heat-laminating process given. Whereas, according to the application by dipping or spraying, it is practically not applicable in view of constraints in production facilities, film formation speed and drying speed in case of plate-shaped large resin substrate. However, such method has problems in production cost, since it requires long drying process after coating, and particularly in case of a resin substrate having a width longer than one meter, a big size drier and long drying process more than 30 minutes are required, which is the cause to make production speed slow and high cost.

#### 【0007】

For carrying a photocatalyst onto a resin structure and a coated resin structure for aiming at providing antifouling, antibacterial and deodorant activity thereto, a method to directly provide a photocatalyst structure which is supporting a photocatalyst layer via an adhesive layer onto the surface of a resin structure or the like can be employed. However, this method requires longer time for drying process after coating than the case of film formation. Namely, in view of heat capacity, at least minute level duration is required for drying when directly forming a film onto a resin structure, whereas only second level duration is enough for drying when taking such film formation process. Therefore, from production efficiency point of view, taking film formation is more advantageous even taking the time required for laminating film into consideration, if the shape of the resin structure is flat sheet-like. This method has another disadvantages such that the resin substrate might be corroded during drying process owing to pH condition of an adhesive layer and a photocatalyst layer and that coating of homogeneous film onto a resin substrate by dipping or spraying to cause the thickness of the film irregular particularly in case that the size of the resin substrate is larger than one meter, thereby giving limitation in the type and size of applicable resin substrates.

#### 【0008】

##### 【Problems to be Solved by the Invention】

It is an object of the present invention to provide resin structures laminated with a photocatalyst-supporting film having excellent deodorant, antifouling, antibacterial, antifungal effects, etc.

**【0009】**

**【Means for Solving Problem】**

It is an object of the present invention to provide a process to efficiently laminate a transparent photocatalyst-supporting film at high speed by heating and a photocatalyst-supporting film of which photocatalytic activity is not inferiorly influenced by heat-laminating process of the photocatalyst-supporting film, which enables to carry on a photocatalyst onto surface of a film which is suitable to give lamination thereon at high speed with good production efficiency. And, the objective is found to be achieved by providing an invention to laminate a polymer resin film having photocatalytic activity, which can decompose triolein at a rate of  $5\mu\text{m}/\text{cm}^2/\text{day}$  or more under irradiation of UV rays in UV-A region at a rate of  $3\text{ mW}/\text{cm}^2$  and at an atmospheric temperature of  $25^\circ\text{C}$  and relative humidity of 70%, onto the surface of a resin substrate by applying heating and pressing.

**【0010】**

Namely, the present invention is related to a resin structure laminated with a photocatalyst-supporting film being obtainable by laminating a photocatalyst-supporting film composed of a polymer resin film, whereto a photocatalyst layer is carried on via an adhesive layer, by applying heating and pressing onto the surface of a resin substrate having photocatalytic activity capable of decomposing triolein at a rate of  $5\mu\text{g}/\text{cm}^2/\text{day}$  or more by irradiating ultraviolet rays in UV-A range at a strength of  $3\text{ mW}/\text{cm}^2$  under condition of atmospheric temperature of  $25^\circ\text{C}$  and relative humidity of 70%.

**【0011】**

The present invention is also related to a resin structure being laminated with the said photocatalyst-supporting film, characterized in that said polymer resin film is one obtained by laminating at least two types of resin films, that the polymer resin is one selected from a group consisting of polycarbonate resins, copolymerization resins of at least two types of polymethylmetacrylate resins and/or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins, that the thickness of the polymer resin film is in a range of from  $5$  to  $200\mu\text{m}$ , that the adhesive layer is formed by coating a coating solution containing a silane coupler as a hardener, that the coating solution

for an adhesive layer is prepared by adding a silane coupler in an amount of 0.1-5% by weight based on the weight of the coating solution as a hardener into a coating solution containing a denaturated silicon resin in an amount of 2-20% by weight based on the weight of the later coating solution, and the denaturated silicon resin contains either 10-50% by weight of polysiloxane or 5-30% by weight of colloidal silica, that the coating solution for an adhesive layer is prepared by adding a silane coupler in an amount of 1-5% by weight based on the weight of the coating solution as a hardener into a coating solution which contains either of monoalkyltrimethoxysilane or its decomposed-product, polysiloxane, in an amount of 1-10% by weight and silica sol in an amount of 0.1-5% by weight based on the later coating solution, that the thickness of the adhesive layer is in a range of from 0.5 to 5  $\mu\text{m}$ , that the photocatalyst-supporting layer contains a metal oxide sol in an amount of 1-10% by weight as a solid component and titanium dioxide sol in an amount of 1-10% by weight as a solid component, that the photocatalyst-supporting layer contains silica sol in an amount of 1-10% by weight, either of monoalkyltrimethoxysilane or its hydrolyzed product in an amount of 1-10% by weight and titanium dioxide sol in an amount of 1-10% by weight, that the thickness of the photocatalyst-supporting layer is in a range of from 0.1 to 5  $\mu\text{m}$ , that the resin substrate is one selected from a group consisting of poly(vinyl chloride) resins, polyethyleneterephthalate resins, polymethylmethacrylate resins, polycarbonate resins, polyethylene resins, polypropylene resins, anti-shock denaturated polystyrene resins and a copolymer of acryl-butadiene-styrene, and that the shape of the resin substrate is plate-like, sheet-like, woven fabric-like, nonwoven fabric-like, resin-containing reinforced fabric-like or tubular.

#### 【0012】

Further, the present invention is related to a process for preparing a resin structure laminated with a photocatalyst-supporting film characterized in that the process is constituted of the first process to coat and then to dry a coating solution for an adhesive layer added with a silane coupler as a hardener onto a polymer resin film, the second process to coat and then to dry a coating solution for a photocatalyst layer onto the adhesive layer to prepare the

photocatalyst-supporting film which carries a photocatalyst layer onto the polymer resin film via the adhesive layer and the third process to laminate the photocatalyst-supporting film onto the surface of a resin substrate by applying heating and pressing.

**【0013】**

Again, the present invention is related to outdoor signboards, telephone boxes, clothes for tents for outdoor use, washstands, modular bathes, systematic kitchens, water tanks for ornamental fishes, plastic cases, wall papers, food trays and films for packaging which are using the resin structure laminated with the photocatalyst-supporting film described above at least as a part of them.

**【0014】**

**【Mode for Carrying Out the Invention】**

The resin structure laminated with a photocatalyst-supporting film is prepared firstly by coating a coating solution for an adhesive layer containing a silane coupler as a hardener onto a film, for example a polymer resin film, then drying the coating solution, and subsequently coating a coating solution for a photocatalyst layer, then drying the coating solution for a photocatalyst layer to prepare a photocatalyst layer on the polymer resin film via an adhesive layer, and then laminating by applying heating and pressing the photocatalyst-supporting film onto the surface of a resin substrate.. The cross section illustration for the inventive resin structure laminated with the photocatalyst-supporting film is shown in Fig. 1.

**【0015】**

For examples of the material used for the polymer resin film specified in the present invention, polycarbonate resins, copolymer resins made of at least two polymethylmetacrylate resins and/or polyacrylate resins, nylon resins, polyamide resins, polyimide resins, polyacrylonitrile resins, polyurethane resins, poly(vinyl chloride) resins, cellophane resins, polyvinylalcohol resins, vinyl acetate-ethylene copolymer resins and ethylene-vinyl alcohol copolymer resins are given. However, it is preferable to use such materials that have both tensile strength and elastic modulus enough to resist to a given tension caused by a film-forming apparatus in order to avoid causing spreads and wrinkles of the film at coating the solution and forming the

photocatalyst layer and the adhesive layer and to obtain a homogeneous and uniform photocatalyst-supporting film.

【0016】

Among the resins as exemplified above, it is particularly preferable to use a film composed of any of polycarbonate resins, copolymers resins made of at least two polymethylmetacrylate resins and/or polyacrylate resins, poly(vinyl chloride) resins and cellophane resins, and the photocatalyst-supporting film using any of these resins has excellent properties in all of photocatalytic activity, durability, film-forming performance, laminating performance, lower cost, etc. Further, the use of a film prepared by laminating two or more of these films described above can greatly improve important properties for a photocatalyst-supporting film, particularly weather-resistance, heat-resistance, moisture permeability, etc. Therefore, it is possible to design and change the property of the photocatalyst-supporting films depending upon the condition where the film is to be used, which is more advantageous for industrial scale production thereof.

【0017】

The thickness of the polymer resin film to be used in the present invention is preferably in a range of from 5 to 200  $\mu\text{m}$ , and the formation of both adhesive layer and photocatalyst layer becomes difficult when the thickness is less than 5  $\mu\text{m}$ , whereas the laminating work becomes difficult and requires higher cost when the thickness is more than 200  $\mu\text{m}$ .

【0018】

The photocatalyst-supporting polymer resin film of the present invention to be used for the lamination onto a resin substrate has a structure wherein an adhesive layer is provided in between the photocatalyst layer and the film, as shown in Fig. 1. The adhesive layer is prepared by coating and then drying a coating solution for an adhesive layer onto the film, which has a role to firmly adhere a photocatalyst layer onto the film and prevents the deterioration of the activity of the photocatalyst caused by a plasticizer component spreading from the film or the polymer resin laminated with the film and degradation of the film due to photocatalytic effect, and the adhesive layer itself has a characteristic being resistant to the

photocatalytic effect.

**【0019】**

For the coating solution for an adhesive layer, the one which contains a silane coupler as a hardener is preferably used. Incorporation of the silane coupler into the coating solution for an adhesive layer enables to accelerate the hardening of the adhesive layer to form a film, which allows to wind the film without causing sticking of the adhesive layer to the reverse side of the film, thereby enabling the formation of the film at high speed. Further, The incorporation of the silane coupler can prevent the deterioration of photocatalytic activity of the photocatalyst-supporting film laminated onto the surface of a resin substrate by means of heating and pressing and allows to maintain the photocatalytic activity owned by the photocatalyst-supporting film before subjecting it to laminating process.

**【0020】**

For an example of the coating solution for an adhesive layer, the one prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight based on the weight of the coating solution containing at a concentration of 2-20% by weight either a silicon denaturated resin containing 10-50% by weight of polysiloxane or a silicon denaturated resin containing 5-30% by weight of colloidal silica, into the coating solution is given.

**【0021】**

In case of using a silicon denaturated resin, such as acrylsilicon resins and epoxysilicon resins, which contains polysiloxane at a concentration of less than 10% by weight, or a silicon denaturated resin which contains colloidal silica at a concentration of less than 5% by weight, for the coating solution for an adhesive layer, adhesivity of the photocatalyst layer at the time of light irradiation gets insufficient, and the adhesive layer decomposes due to photocatalytic effect of outdoor strong ultraviolet rays, whereby easy exfoliation of the adhesive layer is caused. Whereas, in case of using a silicon denaturated resin which contains more than 50% by weight of polysiloxane or more than 30% by weight of colloidal silica, adhesion between the adhesive layer and a carrier structure gets insufficient, the adhesive

layer gets porous, or adhesion between carrier film and the adhesive layer gets insufficient, thereby causing easy exfoliation of photocatalyst layer from the film.

**【0022】**

Further, for an example of the coating solution for an adhesive layer, the one prepared by adding a silane coupler as a hardener in an amount of 0.1-5% by weight based on the weight of the coating solution into a mixture of silica sol and either of monoalkyltrimethoxysilane or the hydrolyzed product, polysiloxane. For examples of the monoalkyltrimethoxysilane, monomethyltrimethoxysilane and monoethyltrimethoxysilane are preferably given. For the silica gel, it is preferable to use the one having the finest primary particle size, and it is particularly preferable to use the one having a primary particle size less than 20 nm for obtaining a transparent film. To the coating solution, it is preferable to incorporate 0.1-5% by weight of silica gel and either of monoalkyltrimethoxysilane or its hydrolyzed product, polysiloxane, at a concentration of 1-10% by weight for obtaining better adhesive property and catalytic activity. The rate for the amount of silica gel and either of monoalkyltrimethoxysilane or the hydrogenated product is preferably in a range of from 20/80 to 60/40, and addition of an acid catalyst, such as mineral acid, may be useful to accelerate hardening.

**【0023】**

The amount of the silane coupler as a hardener to be added is preferably in a range of from 0.1 to 5% by weight based on the weight of the coating solution for an adhesive layer, even though the coating solution is composed of polysiloxane-silicon denaturated resin, colloidal silica-silicon denaturated resin or monoalkyltrimethoxysilane-silica sol. In case that the added-amount of the silane coupler is less than 0.1% by weight, the coated-layer sticks to the reverse side of the film when winding the coated-film following to drying, thereby making subsequent coating of the photocatalyst layer difficult. Whereas, in case that the added-amount of the silane coupler is more than 5% by weight, hardening of the coating solution proceeds too fast or the coating solution gels during the formation of the film. When the silane coupler in an amount of 0.1-5% by weight based on the weight of the

coating solution is applied, photocatalytic activity does not deteriorate, even though the photocatalyst-supporting film is laminated onto the surface of a resin substrate by means of heating and pressing, and the photocatalytic activity can be maintained to the same level as one given before laminating process.

【0024】

For the silane coupler, compounds represented by general formulas,  $\text{RSi(X)}_3$  and  $(\text{R})_2\text{Si(X)}_2$ , wherein R represents an organic functional group and X represents chlorine or alkoxy, can be used, and wherein R represents methyl, ethyl, vinyl,  $\gamma$ -glycidoxypropyl,  $\gamma$ -metacryloxypropyl,  $\gamma$ -(2-aminoethyl)aminopropyl,  $\gamma$ -chloropropyl,  $\gamma$ -mercaptopropyl,  $\gamma$ -aminopropyl,  $\gamma$ -acryloxypropyl or the like and X represents chlorine and  $\text{C}_{1-5}$  alkoxy, such as methoxy, ethoxy and  $\beta$ -methoxyethoxy.

【0025】

Whereas, for a purpose to prevent deterioration of the adhesive layer due to influence of the photocatalytic activity and to improve the durability, a photostabilizing agent and/or an ultraviolet absorbent or the like may be incorporated into the adhesive layer. As usable photostabilizing agents, it is preferable to use hindered amine compounds, however, any other photostabilizing agents can be used as well. Whereas, triazole compounds can be used as the ultraviolet absorbent. The amount of the ultraviolet absorbent to be added into the coating solution is in a range of from 0.005% by weight to 10% by weight based on the weight of the coating solution, and more preferably from 0.01% by weight to 5% by weight. The incorporation of a photostabilizing agent and/or a UV absorbent into the adhesive layer enables to improve the weather resistance of a polymer resin film carrying a photocatalyst, which gives an advantage when it is used at outdoor. In addition, addition of a surface active agent in an amount of 0.00001-0.1% by weight into the coating solution for an adhesive layer enables to get excellent resin structures laminated with the photocatalyst-supporting film.

【0026】

For coating an adhesive layer onto a film, a method to coat a coating solution for an adhesive layer by means of gravure,

microgravure, comma coating, roll coating, reverse roll coating, bar coating, kiss coating and flow coating, then to dry the coating solution can be given. Appropriate temperature during the drying process can be different depending on a coating method, a solvent used, a type of a resin used for a film and thickness of a film, however, it is preferably at 150 °C or less.

【0027】

The thickness of the adhesive layer is preferably 0.5  $\mu\text{m}$  or more. When the thickness is less than 0.5  $\mu\text{m}$ , an effect to firmly adhere the photocatalyst layer onto a film gets insufficient and the photocatalyst layer may exfoliate from the film after long time use. Although it is not a substantial problem to make the adhesive layer thick, however, drying during the formation of the adhesive layer gets insufficient, thereby causing the layer irregular and raising the cost for forming the adhesive layer.

【0028】

The photocatalyst-supporting polymer resin film according to the present invention to be used for lamination onto a resin substrate has a structure that an adhesive layer is provided on a photocatalyst layer, as shown in Fig.1. The photocatalyst layer can be formed by coating a coating solution for photocatalyst layer which, for example, contains 1-10% by weight of metal oxide sol as solid component and 1-10% by weight of titanium dioxide sol as solid component and then drying the solution. The metal oxide sol contained in the coating solution for a photocatalyst layer works not only to fix the titanium dioxide sol and firmly adhere it to an adhesive layer but also to enhance photocatalytic activity owing to its absorption property based on the porous structure of the gel obtained by drying the metal oxide sol. Ratio of the metal oxide sol and the titanium dioxide sol in the coating solution for a photocatalyst layer is preferably in a range of from 25/75 to 95/5. Adhesion to the adhesive layer gets insufficient when the ratio of the metal oxide sol is less than 25%, whereas photocatalytic activity gets insufficient when the ratio is more than 95%. Further, when the specific surface area of the gel that is obtained by drying the metal oxide sol is 100  $\text{m}^2/\text{g}$  or more, the adhesivity get more firm as well as improvement in the photocatalytic activity. For an example of the metal

in the metal oxide sol, silicon, aluminium, titanium, zirconium, magnesium, niobium, tantalum and tungsten are preferably given, and mixtures of these metal oxide sol and complex oxide sols prepared by coprecipitation method, etc. can be used as well.

【0029】

When mixing a metal oxide sol with titanium dioxide sol, it is preferable to mix it in sol state or in a state being at before preparing into the sol. As a method to prepare the sol, a method to hydrolyze the metal salt, a method to decompose it under neutral condition, a method to subject it to ion exchange, a method to hydrolyze the metal alkoxide, etc. can be given, however, any methods which allow to obtain the sol wherein titanium dioxide sol is homogeneously distributed can be employed. However, it is more preferable to use a sol which contains less impurities since such impurities in greater amount in the sol may give unfavorable effects on adhesivity of a photocatalyst and its photocatalytic activity. In particular, when organic substance in an amount more than 5% by weight relative to the dry weight of the sol is contained in the sol, photocatalytic activity may be decreased. Particularly, it is more preferable to use zirconium oxide sol or aluminium oxide sol to prepare a photocatalyst layer, since it may facilitate to get through tape exfoliation tests after having either 15 min. resistance test to boiling water or dipping test for 168 hours into 5% sodium carbonate solution.

【0030】

Whereas, it is particularly preferable to use a coating solution for a photocatalyst layer which is composed of a mixture of silica sol in an amount of 1-10% by weight, either monoalkyltrimethoxysilane or its hydrolyzed-product in an amount of 1-10% by weight and titanium dioxide sol in an amount of 1-10% by weight for coating onto an adhesive layer to obtain a photocatalyst layer. For the monoalkyltri-methoxysilane, it is more preferable to use methyltrimethoxysilane and methyltriethoxysilane. The ratio to mix silica sol with either monoalkyltrimethoxysilane or its hydrolyzed-product, it is preferable to select a rate by weight of from 100/0 to 60/40, whereas as a rate by weight of titanium dioxide sol to a silane compound, it is preferable to use a ratio of from 5/95 to 75/25. In case that the ratio for the

silane compound is more than 95, photocatalytic activity may be decreased, while adhesivity to an adhesive layer may be decreased when the ratio is lower than 25.

【0031】

For the photocatalyst in a photocatalyst layer,  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{SrTiO}_3$ ,  $\text{CdS}$ ,  $\text{GaP}$ ,  $\text{InP}$ ,  $\text{GaAs}$ ,  $\text{BaTiO}_3$ ,  $\text{K}_2\text{NbO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{WO}_3$ ,  $\text{SnO}_2$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{NiO}$ ,  $\text{Cu}_2\text{O}$ ,  $\text{SiC}$ ,  $\text{SiO}_2$ ,  $\text{MoS}_2$ ,  $\text{InPb}$ ,  $\text{RuO}_2$ ,  $\text{CeO}_2$ , etc. can be given. Further, any photocatalysts as exemplified above where to a metal, such as  $\text{Pt}$ ,  $\text{Rh}$ ,  $\text{RuO}_2$ ,  $\text{Nb}$ ,  $\text{Cu}$ ,  $\text{Sn}$  and  $\text{NiO}$ , and their oxide compounds, is incorporated can be also used. The content of a photocatalyst in a photocatalyst layer is preferably lower than 75% by weight in view of adhesivity, though photocatalytic activity increase along with increase of the content. In order to further improve antibacterial and antifungal activities, it is also useful to incorporate a metal or a metallic compound in an amount of 0.05-5% by weight relative to the weight of titanium dioxide photocatalyst in a photocatalyst layer. When the incorporated-amount of such metal compound is less than 0.05% by weight, the improving effect on antibacterial and antifungal activity is poor, while discoloration of a photocatalyst layer may be caused when the incorporated-amount of a metal compound is more than 5% by weight, which may give constrain to use such a photocatalyst layer depending upon the color or design of a resin structure laminated with a film.

【0032】

For the formation of a photocatalyst layer on an adhesive layer, a suspension wherein a photocatalyst is dispersed in either a metal oxide sol or a metal hydroxide sol can be used according to the coating method as described above in the formation of an adhesive layer. Alternatively, a photocatalyst can be dispersed in a precursor solution of such metal oxide or metal hydroxide, then to prepare sol or gel of such metal oxide or metal hydroxide by subjecting them to hydrolysis or decomposition under neutral condition at coating. When such sol is used, a deflocculant, such as an acid and an alkali, may be added for stabilizing the sol suspension. By adding a surface active agent or a silane coupler in an amount of 5% by weight relative to the weight of a photocatalyst into the sol suspension to improve adhesivity and

handling efficiency. However, the addition of a silane coupler into a photocatalyst layer cannot prevent decrease in photocatalytic activity at a process to laminate a photocatalyst-carrying film onto the surface of a resin substrate by applying heating and pressing and facilitate to maintain the photocatalytic activity owned by a photocatalyst-supporting film before the laminating process. Temperature at forming a photocatalyst layer is preferably 150 °C or lower, though appropriate temperature may differ depending upon coating method, a material used for a film or resin type of an adhesive layer.

【0033】

The photocatalytic activity increases along with the increase of thickness of a photocatalyst layer, however, in a range more than 5  $\mu\text{m}$ , no more increase of photocatalytic activity is recognized. The photocatalyst layer having thickness less than 5  $\mu\text{m}$  shows high photocatalytic activity, still has light permeability and makes a photocatalyst layer less distinguish, whereas the photocatalyst layer in less than 0.1  $\mu\text{m}$  thick has high light permeability, but it allows ultraviolet rays to be utilized by a photocatalyst passing therethrough, whereby unabling to obtain high photocatalytic activity. High photocatalytic activity can be obtained by making the thickness of a photocatalyst layer to a range of from 0.1 to 5  $\mu\text{m}$  and using a photocatalyst crystals having a particle size of 40 nm or less and either a metal oxide gel or a metal hydroxide gel having a specific surface area of 100 $\text{m}^2/\text{g}$  or more. In this case, it is also favorable to use such photocatalyst layer in view of picture because it does not defile the appearance of a resin substrate to which a base film is laminated.

【0034】

For the resin substrate to be laminated with a photocatalyst-supporting film by heating and pressing according to the present invention, the ones made of a resin selected from a group consisting of poly(vinyl chloride)resins, polyethyleneterephthalate resins, polymethylmetacrylate resins, polycarbonate resins, polyethylene resins, polypropylene resins, denaturated polystyrene resins, shock-resistant polystyrene resins and acryl-butadiene-styrene copolymer resins can be given as examples. As to the shape of the resin substrate, plate-like,

sheet-like, fabric-like, unwoven fabric-like, resin-reinforced fabric-like, tubular and the like can be given, and any shape which allows to laminate the photocatalyst-supporting film of the present invention onto them can be applicable.

【0035】

As a method to laminate the photocatalyst-supporting film onto various types of resin substrates, a method to laminate the film onto a resin substrate, such as a resin plate and a paint-coated resin plate, while heating and pressing the film by using a heated roller or the like, a method to laminate a photocatalyst-supporting polymer resin film by heating and pressing, which utilizes heat being applied during manufacturing of resin substrates, onto a resin substrate, such as a resin plate, a painted resin plate and a resin-coated resin plate, are preferably used because these methods allow industrially efficient manufacturing. For the lamination of the photocatalyst-supporting film by applying heating and pressing onto a resin substrate, it is preferable to employ a laminating method by short time heating normally at a temperature of from 60 to 200°C though it depends on the material of the resin used for the base film, a laminating method to press the film by utilizing heat arising at kneading a resin to be used for a resin substrate, a laminating method by passing through a heated roller or subjecting to hot press and the like can be preferably employed.

【0036】

In addition, it is further possible to increase the film adherence and durability of laminated-products by subjecting the surface of a resin substrate, whereto heating and pressing process is applied, to corona discharge and ultraviolet radiation and by using a structure on which any of acryl-type, urethane-type and epoxy-type adhesives is coated as a primary layer. Further, it is still feasible to obtain resin structures which has long durability for the use and can keep excellent photocatalytic activity by selecting an appropriate temperature, pressure and time corresponding to the material of a resin substrate, such as a resin plate and a paint-coated resin plate, and the materials used for the photocatalyst-supporting film. Again, according to the present invention, very firm adherence between a photocatalyst layer and an adhesive layer can be gained by applying

products by using a base structure obtainable by coating and drying a acryl-type, urethane-type or epoxy-type sticker as a primer layer onto the surface of the metal plate to be subjected to heating and pressing.

For the heating and pressing of the photocatalyst-supporting film onto the surface of a base structure, a method to pass through a heated roller or to subject to heat-pressing and the like can be employed. In this case, a metallic plate, which can keep its durability and photocatalytic activity even it has been used for a long time, can be obtained by selecting appropriate temperature, pressure and time suitable for the material of a metallic plate or a paint-coated metallic plate, etc. to be used as a structure and the material of the film used for the photocatalyst-supporting film. In the present invention, heating and pressing are employed for the laminating process, which allows to establish firm sticking of the photocatalyst layer to the adhesive layer and to obtain better durability, adherence and anti-exfoliation property than those before subjecting them to heating and pressing process.

【0037】

The metallic plate laminated by heating and pressing with the photocatalyst-supporting film of the present invention are the one which can degrade triolein at a rate of more than  $5 \mu\text{g}/\text{cm}^2/\text{day}$  when irradiating ultraviolet rays in UV-A region (400–315 nm) at a strength of  $3 \text{ mW}/\text{cm}^2$  under an atmospheric temperature of  $25^\circ\text{C}$  and relative humidity of 70%. Some of the metallic plate laminated with the photocatalyst-supporting film of the present invention shows high durability represented by photocatalyst layer adherence point of 6 or higher according to JIS cross-cut adhesion test method K 5400, even after irradiating black light of  $3 \text{ mW}/\text{cm}^2$  as ultraviolet ray strength for 1,000 hours under a temperature of  $40^\circ\text{C}$  and relative humidity of 90%.

【0038】

The photocatalyst-supporting film of the present invention provided with an adhesive layer and a photocatalyst layer can be produced at high production efficiency as fast as several ten meters per minute, and lamination of this film onto various metallic plates can be accomplished as fast as a rate of several meters per minute if conditions for the process is well optimized. Accordingly, the present

invention has big advantage in improvement in production efficiency and quality, such as homogeneity of film thickness, which are facilitated by quite faster formation of a photocatalyst layer comparing to the fastness in the method to coating and drying a photocatalyst layer onto metallic plates according to common dipping method or spraying method. Further, the metallic plates laminated with the photocatalyst-supporting film of the present invention has quite a wide application range since those structures can be prepared into various shapes by molding of metallic plates by press processing following to lamination with the photocatalyst-supporting film and subsequent cutting.

【0039】

The metallic plates laminated with the photocatalyst-supporting film of the present invention are widely used as materials for general buildings and outdoor constituted bodies. For examples, the metallic plates can be used for constituted structures along roads, such as soundproof boards for motorway, street-side telephone boxes, road signs and guardrails, metallic plates used in bathrooms, toilets, kitchens, cuisines, etc., commodes, modular bathes, system kitchens, toilet bowls, various sinks, etc.

【0040】

The metallic plate laminated with the photocatalyst-supporting film of the present invention is advantageously used for parts where deodorant, antifouling, antibacterial and antifungal effects are required, such as outdoor advertisement boards, walls for transportation vehicles like trains and buses, walls of food factories and feeding facilities, frames for home-use electric appliances, such as refrigerators, washing machines, personal computers, radios and TV, various types of illumination reflectors, interior walls for cooling warehouses and freezing warehouses, and the surface of those which products are kept clean for a long time because of the excellent antifouling, oil-decomposing, antibacterial and antifungal effects of the inventive photocatalyst-supporting film.

【0041】

When the metallic plate laminated with the inventive photocatalyst-supporting film is used for outdoor advertisement boards, traffic signs and guardrails, soot and lampblack contained in exhaust or the like are

decomposed by the film, thereby facilitating removal by wind and raining of dust, sand and clay being attached to the surface of the metallic plate thanks to the adhering effect of soot and lampblack, which eventually give antifouling effect to the metallic plate. When stainless steel plate laminated with the photocatalyst-supporting film of the present invention is used for illumination reflectors, interior oil mist and cigarette smoke attached to the reflectors can be decomposed thanks to ultraviolet rays irradiated from a fluorescent lamp to reduce oily smirch on the surface. Further, when the stainless steel plate laminated with the photocatalyst-supporting film of the present invention is used for frames for home-use electric appliances, such as refrigerators, radios and TV, though amount of ultraviolet rays irradiated to interior is small, interior floating oil mist and hand wax components given by finger touch are gradually decomposed by the photocatalyst action, thereby reducing attached hand wax and dark smirch to the surface.

【0042】

【Examples】

Now, the present invention is definitely explained with referring the examples described below, however, the scope of the present invention should not be limited to the range described in such examples.

Example 1: Preparation of photocatalyst-supporting film

A coating solution for an adhesive layer and a coating solution for a photocatalyst layer were coated onto an acryl resin film (Mitsubishi Rayon Co., Ltd., Acryprene HBS-006) having a thickness of  $50\mu\text{m}$  by using microgravure printer (Yasui Seiki Co., Ltd.). To ethanol-ethyl acetate solution (50/50 ratio by weight) which contains an acrylsilicon resin contains 3 mol% silicon in an amount of 8% by weight as solid component, 20% ethanol solution of methylsilicate MS 51 (Colcoat Co., Ltd.) as polysiloxane in an amount of 35% by weight as solid component relative to the weight of said acrylsilicon resin and  $\gamma$ -glycidoxypropylmethoxysilane in an amount of 1% by weight were added to prepare a coating solution for an adhesive layer. An adhesive layer was formed at a speed of 20 m/min. and at 60 °C, and then cooled under a room temperature. In the presence of a surface active agent, an equivalent of a solution

prepared by dispersing acidic silica sulfate sol so as to contain silica oxide at a concentration of 10% by weight into water-ethanol solution (50/50 ratio by weight) was added to a solution wherein acetic titanium sulfate is dispersed so as to contain titanium dioxide at a concentration of 10% by weight into water-ethanol solution (50/50 ratio by weight) to prepare a coating solution for a photocatalyst layer. A photocatalyst layer was formed with this coating solution according to the same procedures as described above for preparing the adhesive layer to obtain a photocatalyst-supporting film (A). According to the same procedures, other photocatalyst-supporting films were prepared by coating an adhesive layer and a photocatalyst layer onto an acryl-type film (Kanegafuchi Kagaku Co., Ltd., Sandulene 008NCT) having a thickness of  $50\mu\text{m}$  (film B) and hard-type vinyl chloride film having a thickness of  $50\mu\text{m}$  (film C) under different temperature and drying condition.

【0043】

Example 2: Preparation of an iron plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (A) obtained in Example 1 was attached onto the surface of an iron plate in 1 mm thick being cut to a dimension of 5 cm x 5 cm, whereto an acryl-type adhesive as a primer is coated and dried, and the iron plate was subjected to air evacuation by applying pressure for 10 sec. at a degree of  $50\text{ kg/cm}^2$  five times at  $120^\circ\text{C}$ . The iron plate was further heated and pressed for 2 min. at the same temperature and at a degree of  $50\text{ kg/cm}^2$ , for 2 min. at  $100\text{ kg/cm}^2$ , and for 1 min. at  $150\text{ kg/cm}^2$ , and then cooled down to below  $50^\circ\text{C}$  while applying pressure to obtain an iron plate laminated with a photocatalyst-supporting film. (Sample 1)

【0044】

Example 3: Preparation of an aluminium plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (A) obtained in Example 1 was attached onto the surface of an aluminium plate in 1 mm thick being cut to a dimension of 5 cm x 5 cm, whereto an acryl-type adhesive as a primer is coated and dried, to obtain an aluminium plate laminated with a photocatalyst-supporting film according to the same laminating procedures as described in Example 2. (Sample 2)

**【0045】**

Example 4: Preparation of a stainless steel plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (A) obtained in Example 1 was attached onto the surface of a stainless steel plate (SUS-304) in 1 mm thick being cut to a dimension of 5 cm x 5 cm, where to an acryl-type adhesive as a primer is coated and dried, to obtain a stainless steel plate laminated with a photocatalyst-supporting film according to the same laminating procedures as described in Example 2. (Sample 3)

**【0046】**

Example 5: Preparation of a paint-coated steel plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (B) obtained in Example 1 was laminated onto a heat-coated steel plate with an acryl-type paint having a thickness of 0.3 mm, a width of 60 cm and a length of 1 m by using a heat-pressing type laminating roller under condition of nipping pressure of 5 kg/cm, sheet surface temperature of 150°C at laminating roller point and sheet feeding speed of 10 m/min. to prepare a coated steel laminated with a photocatalyst-supporting film. This laminated, paint-coated steel plate was cut to a dimension of 5 cm x 5 cm to obtain a sample to provide for tests. (Sample 4)

**【0047】**

Example 6: Preparation of a paint-coated aluminium plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (B) obtained in Example 1 was attached to a paint-coated aluminium plate in 1 mm thick and cut to a dimension of 5 cm x 5 cm, where to an acryl-type coating material is heat-coated, and was processed according to the same procedures as described in Example 2 to obtain a paint-coated aluminium plate laminated with a photocatalyst-supporting film. (Sample 5)

**【0048】**

Example 7: Preparation of a vinyl chloride-coated steel plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (C) obtained in Example 1 was attached to a vinyl chloride-coated steel plate in 1 mm thick and cut to a dimension of 5 cm x 5 cm, and the attached-steel plate was then

subjected to pressing 4-5 times for each 10 seconds at a pressure of 50 kg/cm<sup>2</sup> to complete air evacuation. Then, the attached steel plate was subjected to heating and pressing for 30 seconds at the same temperature and pressure of 50 kg/cm<sup>2</sup>, for 1 min. at 100 kg/cm<sup>2</sup> and for 30 seconds at 150 kg/cm<sup>2</sup> and then cooled down to below 50 °C while pressing to obtain a vinyl chloride-coated steel plate laminated with a photocatalyst-supporting film. (Sample 6)

【0049】

Example 8: Preparation of a polyester-coated steel plate laminated with a photocatalyst-supporting film

The photocatalyst-supporting film (C) obtained in Example 1 was attached to a polyester-coated steel plate in 1 mm thick and cut to a dimension of 5 cm x 5 cm according to the same procedures as described in Example 7 to obtain a polyester-coated steel plate laminated with a photocatalyst-supporting film. (Sample 7)

【0050】

Example 9: Preparation of an iron plate laminated with a copper-added photocatalyst-supporting film

In the presence of a surface active agent, the equivalent amount of water-ethanol solution composed in 50/50 ratio by weight, whereto acidic silica nitrate sol is dispersed so as to contain silica oxide sol in an amount of 10% by weight, is added to water-ethanol solution composed of 50/50 ratio by weight, whereto acidic titanium nitrate sol is dispersed so as to contain titanium dioxide in an amount of 10% by weight. To the resulting mixture, copper nitrate hydrate was added and dissolved so as to be a concentration of 0.1% by weight based on metal copper relative to titanium dioxide, and a photocatalyst-supporting film coated with an adhesive layer and a photocatalyst layer was prepared by using same film, same materials and same procedures as employed for preparing the fil (A) described in Example 1 except the preparation process of the coating solution for a photocatalyst layer. The photocatalyst-supporting film prepared here above was attached with an iron plate in 1 mm thick and cut to a dimension of 5 cm x 5 cm according to the same procedures as described in Example 2 to obtain an iron plate laminated with a copper-added photocatalyst-supporting film. (Sample 8)

【0051】

Example 10: Reflection plates for lighting fixtures

A reflection plate for fluorescence lamp is produced by using a coated steel plate laminated with the photocatalyst-supporting film prepared in Example 5. The reflection plate was then cut into a piece having a dimension of 5 cm x 5 cm to prepare a sample for property evaluation. (Sample 9)

【0052】

Example 11: Outdoor signboards

A outdoor signboard is prepared by using a coated steel plate laminated with the photocatalyst-supporting film prepared in Example 5.

The evaluated rank of the outdoor signboard using the prepared steel plate laminated with the photocatalyst-supporting film for antifouling effect conducted according to a method described later was A. On the other hand, antifouling effect of a steel plate laminated with a film without carrying a photocatalyst was evaluated as D rank.

【0053】

Example 12: Refrigerator

A box to be used for a vegetable container for a refrigerator was prepared by using a iron plate laminated with the photocatalyst-supporting film prepared in Example 9. Three fluorescence lamps for photocatalyst, Ecoclean (FC2BLB/200T12) manufactured by Toshiba Laitec was lighten in the box, and 5 carrot fruits, 2 cabbage rolls, 10 tomato fruits, 10 cucumber fruits, 1 bundle of spinach and 10 green pepper fruits were directly placed in the box, and each placed vegetables in same number were replaced with new ones every 3 days. Another box in same size was prepared by using an iron plate laminated with a film carrying no photocatalyst, and three fluorescence lamps for photocatalyst, Ecoclean (FC2BLB/200T12) manufactured by Toshiba Laitec was lighten in the box, and same variety and number of vegetables were placed in the box. Each f the placed vegetables were replaced with new ones in same number every 3 days. As a result, almost no mold and stain were recognized for the box prepared by using the iron plate laminated with the photocatalyst-supporting film. Contrary, remarkable mold growth and stains were recognized in the box prepared by using an iron plate laminated with a film carrying no photocatalyst.

【0054】

Example 13: Guardrails

A guardrail was prepared by using a coated steel plate laminated with the photocatalyst-supporting film prepared in Example 5 to examine its antifouling property, for which method is described later. Similarly, another guardrail prepared by using a coated steel plate laminated with a film carrying no photocatalyst was prepared to compare its antifouling property. As a result, antifouling property of the guardrail made of the coated steel plate laminated with the photocatalyst-supporting film was evaluated as A, whereas antifouling property of the one made of the coated plate laminated with the film carrying no photocatalyst was evaluated as D.

【0055】

Example 14: Road signs

A signboard having a similar size as that of a road sign was prepared by using a coated steel plate laminated with the photocatalyst-supporting film prepared in Example 5 to evaluate its antifouling property, for which method is described later. Another road sign having a same size prepared by using a coated steel plate laminated with a film carrying no photocatalyst was prepared to compare its antifouling property. As a result, antifouling property of the road sign prepared by using the coated steel plate laminated with the photocatalyst-supporting film was evaluated as A, whereas antifouling property of the road sign prepared by using the coated steel plate laminated with the film carrying no photocatalyst was evaluated as D.

【0056】

Example 15: Durability evaluation on a laminated steel plate

The guardrail prepared in Example 13 was installed outdoor for a year, and adhesion property of the guardrail was then checked at ten different places according to the criterion as described later. The adhesion property of the guardrail was evaluated as 8 points at 4 places and 10 points at 6 places.

【0057】

Reference Example 1

Acryl resin film, Acryplane HBS-006, manufactured by Mitsubishi Rayon Co., Ltd. indicated in Example 1 having 50  $\mu$ m thickness was

attached to an iron plated cut to a dimension of 5 cm x 5 cm to prepare an iron plate laminated with PET film.

【0058】

#### Reference Example 2

Acryl resin film, Acryplane HBS-006, manufactured by Mitsubishi Rayon Co., Ltd. indicated in Example 1 having 50  $\mu$ m thickness was attached to a steel plate coated by means of baking coating with acryl-type coating cut to a dimension of 5 cm x 5 cm to prepare a coated steel plate laminated with an acryl film according to the same method and conditions indicated in Example 2.

【0059】

#### Reference Example 3

Hard vinyl chloride film manufactured by Sumitomo Bakelite Co., Ltd. indicated in Example 1 in 50 $\mu$ m thick was attached to a steel plated in 1 mm thick coated with vinyl chloride and cut to a dimension of 5 cm x 5 cm to prepare a steel plate laminated with vinyl chloride film according to the same method and conditions indicated in Example 5.

【0060】

#### (Evaluation on Photocatalytic Activity)

Evaluations on photocatalytic activity as described below were conducted by using samples No. 1 through 9 and samples for reference examples. The results are shown in Table 1.

【0061】

#### 1) Antifouling property

A sample being cut to a dimension of 5 cm x 5 cm was placed onto a fence facing to a road (traffic frequency: c.a. 500-1,000 tracks per day) along with a blank sample in same size with no photocatalyst. After 3 months, fouling degree on the surface of the test samples and the blank samples were compared by using a spectral colorimeter based on a check sample kept in a dark and cool room according to the criterion shown below.

| Degree of discoloration increase ( $\Delta E$ )<br>after 3 months | Evaluated rank |
|---|----------------|
| 5 or less   | A              |
| 5-10  | B              |
| 10-20   | C              |

## 【0062】

## 2) Triolein-decomposing Property (Oil-decomposing Activity)

Triolein (Highest reagent grade, Wako Pure Chemical) in an amount of 0.1 mg/cm<sup>2</sup> was coated onto a test sample being cut to a dimension of 5 cm x 5 cm by using tissue paper (Kimwipe), and the sample was then placed in a container maintained at 25 °C and 70% R.H. The sample in the container was then subjected to irradiation with commercially-available 15W black light fluorescence lamp by adjusting a distance between the light source and the sample surface so as to receive UV light in UV-A region at strength of 3 mW/cm<sup>2</sup> at a surface point of the sample. Reducing amount of triolein relative to light irradiation time was measured by using a precision balance to determine triolein-decomposing activity according to the criterion shown below.

| Remaining rate of Triolein<br>after 5 days (%) | Evaluated rank                              |
|--|---|
| 10% or lower                                   | A (18 $\mu$ g/cm <sup>2</sup> /day or more) |
| 50%-10%  | B (10-18 $\mu$ g/cm <sup>2</sup> /day)      |
| 75%-50%  | C (5-10 $\mu$ g/cm <sup>2</sup> /day)       |
| 95%-75%  | D (1-5 $\mu$ g/cm <sup>2</sup> /day)        |
| 95% or more                                    | E (1 $\mu$ g/cm <sup>2</sup> /day or less)  |

## 【0063】

## 3) Antibacterial Activity

A sample being cut to a dimension of 5 cm x 5 cm was disinfected with 80% ethanol and dried at 150 °C. Consequently, bacterial solution of E. coli in an amount of 0.2 ml, which is cultured and diluted to a concentration of 10<sup>5</sup> bacteria/ml beforehand, was fed dropwise onto the surface of the sample and placed in an incubator. For this evaluation test, each 4 samples were provided for two different lighting conditions, one case where irradiation of white fluorescence lamps (15W x 2 lamps, distance between a lamp and the sample, 10 cm) was done and the other case where no irradiation of white fluorescence lamp was given. After predetermined intervals, which are 1, 2, 3 and 4 hours later, respectively, the samples were taken out from the incubator, and the bacterial solution on the sample was removed with disinfected gauze dipped in disinfected physiological saline solution, and the gauze was

then put into 10 ml disinfected physiological saline solution and thoroughly stirred. Supernatant obtained was then inoculated to agar medium in a petri dish having a diameter of 95 mm, which is disinfected by autoclave beforehand, and was kept for culturing under a temperature of 36 °C for 24 hours for counting colonies of E. coli. On the other hand, a sample for counting bacteria for check was prepared according to the same procedures, and supernatant of bacterial solution in disinfected saline solution was inoculated to agar medium in a petri dish and kept for 24 hours to grow for subsequent counting of E. coli colonies. Based on the numbers of E. coli colonies obtained, livability of E. coli after pre-determined intervals was calculated for each conditions, respectively. Evaluation was carried out base on the livability of E. coli at 4 hours after starting irradiation of fluorescence lamp, and the following criterion was applied to evaluate.

| Livability of E. coli after 4 hours | Evaluated rank |
|-------------------------------------|----------------|
| 20% or lower                        | A              |
| 20-40%                              | B              |
| 40-60%                              | C              |
| 60-80%                              | D              |
| 80% or more                         | E              |

【0064】

4) Antifungal activity

Degree of green mold grown on the surface of the sample for evaluation of antifouling property was compared according to the following criterion with the samples having been kept in a dark and cool room.

| Degree of grown mold on Sample Surface | Evaluated rank |
|--|----------------|
| Almost no growth                       | A              |
| Little growth recognized on a part     | B              |
| Growth recognized remarkably           | C              |

【0065】

(Evaluation on Adhesivity)

According to cross-cut adhesion test provided in JIS K 5400, adhesivity of the samples were evaluated. Distance of each cut was set to 2 mm and number of squares was set to 25. Evaluation was accorded to the criterion described in JIS K 5400.

【0066】

(Evaluation of Durability)

The photocatalyst-supporting samples were allowed to irradiation of black light at ultraviolet ray intensity of 3 mW/cm<sup>2</sup> for 1,000 hours in a container maintained at 40°C and 90% R.H., then the samples were subjected to cross-cut adhesivity test provided in JIS K 5400 to evaluate their durability. Evaluation was accorded to the criterion described in JIS K 5400.

【0067】

【Table 1】

| Sample No. | Anti-fouling activity | Oil-decomposing activity | Anti-bacterial activity | Anti-fungal activity | Adhesivity | Durability |
|------------|-----------------------|--------------------------|-------------------------|----------------------|------------|------------|
| Sampl. 1   | B                     | A                        | B                       | B                    | 10         | 10         |
| 2          | B                     | A                        | B                       | B                    | 10         | 10         |
| 3          | B                     | A                        | B                       | B                    | 10         | 10         |
| 4          | B                     | B                        | B                       | B                    | 10         | 10         |
| 5          | B                     | B                        | B                       | B                    | 10         | 10         |
| 6          | B                     | C                        | B                       | B                    | 10         | 10         |
| 7          | B                     | C                        | B                       | B                    | 10         | 10         |
| 8          | B                     | A                        | A                       | A                    | 10         | 10         |
| 9          | B                     | B                        | B                       | B                    | 10         | 10         |
| Ref. 1     | D                     | E                        | E                       | C                    | —          | —          |
| 2          | D                     | E                        | E                       | C                    | —          | —          |
| 3          | D                     | E                        | E                       | C                    | —          | —          |
| 4          | D                     | D                        | C                       | C                    | 10         | 6          |

【0068】

Reference Example 4

According to Example 48 described in WO 97-134, a coating solution for an adhesive layer was prepared by adding cataroid SI-350 (Shokubai Kasei Co., Ltd.) into aqueous acrylsilicon resin emulsion containing 20% silicon so as to adjust the content of SiO<sub>2</sub> in the dried adhesive layer at 10%, thereby adjusting the content of whole dry solid components to 20%. On the other hand, a coating solution for a photocatalyst layer was prepared so as to contain titanium dioxide P-25 for photocatalyst-use (Nihon Aerosil Co., Ltd.) at a content of 30% as

solid component, Silica zol cataroid SI-30 (Shokubai Kasei Co., Ltd.) at a content of 20% as solid component, Alumina zol-200 (Nissan Chemical Industries Co., Ltd.) at a content of 10% as dry solid component, acrylsilicon resin emulsion containing 20% by weight silicon at a content of 35% as nonvolatile residue and tri( $\beta$ -methoxyethoxy) vinylsilane (Nihon Uniker Co., Ltd.) as a silane coupler at a content of 5% as nonvolatile component and so as to make the content of whole dry residue at 10%. Though application of coating was carried out by using these coating solutions onto acryl film in 50 $\mu$ m thick, Acryplane HBS-006, manufactured by Mitsubishi Rayon by using microgravure printer (Yasui Seiki Co., Ltd.), film coating was not successful due to insufficient drying and hardening of the adhesive layer. Alternatively, such coating was tried by using the same coating solutions for an adhesive layer and a photocatalyst layer onto the acryl film (Mitsubishi Rayon Co., Ltd.) indicated above by using a desk bar coater, and the coated film was then dried at 80°C, however, 1 hour time was required to dry the coated film. The acryl film carrying a photocatalyst was attached to the surface of polyester resin-coated steel plate cut to a dimension of 5 cm x 5 cm and subjected to heat lamination process according to the same method and conditions indicated in Example 2. Antifouling, oil-decomposing, antibacterial, and antifungal property, adhesivity, and durability of the polyester resin-coated steel plate heat-laminated with the photocatalyst-supporting film were shown in Table 1, which demonstrates its inferiority in oil-decomposing property, durability, etc. As explained above, application of the photocatalyst-supporting film prepared by using a coating solution for an adhesive layer containing no silane coupler therein was found to be inadequate.

【0069】

#### 【Effects of the Invention】

The metallic plates laminated with a photocatalyst-supporting film according to the present invention are useful as materials for exterior construction materials, interior building materials, structures along roads, outdoor signboards, outdoor signs, home-use electric appliances, various lighting equipments, and goods and installations used in cuisine, kitchens, toilets, and bathroom, etc., which require higher photocatalytic activity, excellent durability, and antifouling,

antibacterial and antifungal properties, and are advantageous in view of cost-performance comparison. The photocatalyst-supporting film of the present invention provided with an adhesive layer and a photocatalyst layer can provide high productivity and fast film formation at a speed more than several tens meters per minute, and additionally, at laminating process of the photocatalyst-supporting film onto various metallic plates, it is possible to facilitate faster film formation at a speed of more than several tens meters per minute by optimizing the conditions during the process.

【Brief Explanation of Drawings 】

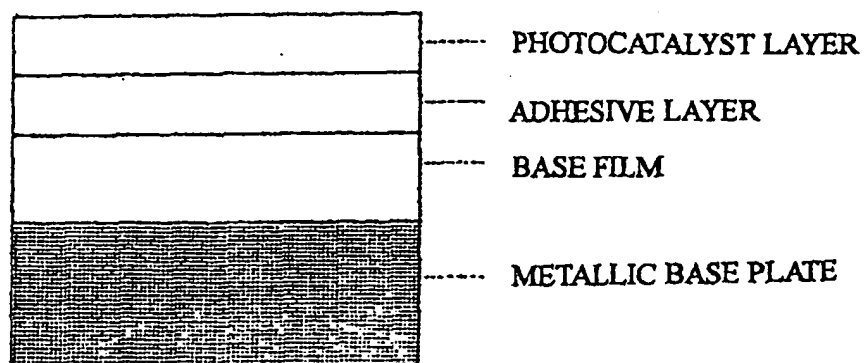
【Fig. 1】

This is a model diagram for a cross section of a resin body laminated with the photocatalyst-supporting film according to the present invention.

【Type of Document】

Figure

【Fig. 1】



【Type of Document】 Abstract of the Disclosure

【Summary】

【Problem】 To provide a metallic plate, a resin-coated metallic plate, paint-coated metallic plate and an enamelled metallic plate laminated with a photocatalyst-supporting film having excellent deodorant, antifouling, antibacterial and antifungal activity, etc.

【Means for Solving Problem】 To provide a metallic plate laminated with a photocatalyst-supporting film which is prepared firstly by coating a coating solution for an adhesive layer containing a silane coupler as a hardener onto a polymer resin film, then drying the coating solution, and subsequently coating a coating solution for a photocatalyst layer, then drying the coating solution for a photocatalyst layer to prepare a photocatalyst layer on the polymer resin film via an adhesive layer, and then laminating by heating and pressing the photocatalyst-supporting film onto the surface of the metallic plate.